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PRELIMINARY EVALUATION OF A HALOGEN LEAK DETECTOR  
FOR SCREENING DIVERS' BREATHING AIR

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## TECHNICAL REVIEW AND APPROVAL

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The experiments reported herein were conducted according to the principles set forth in the current edition of the "Guide for the Care and Use of Laboratory Animals," Institute of Laboratory Animal Resources, National Research Council.

This technical report has been reviewed by the NMRI scientific and public affairs staff and is approved for publication. It is releasable to the National Technical Information Service where it will be available to the general public, including foreign nations.

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CAPT, MC, USN

Commanding Officer  
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## INTRODUCTION

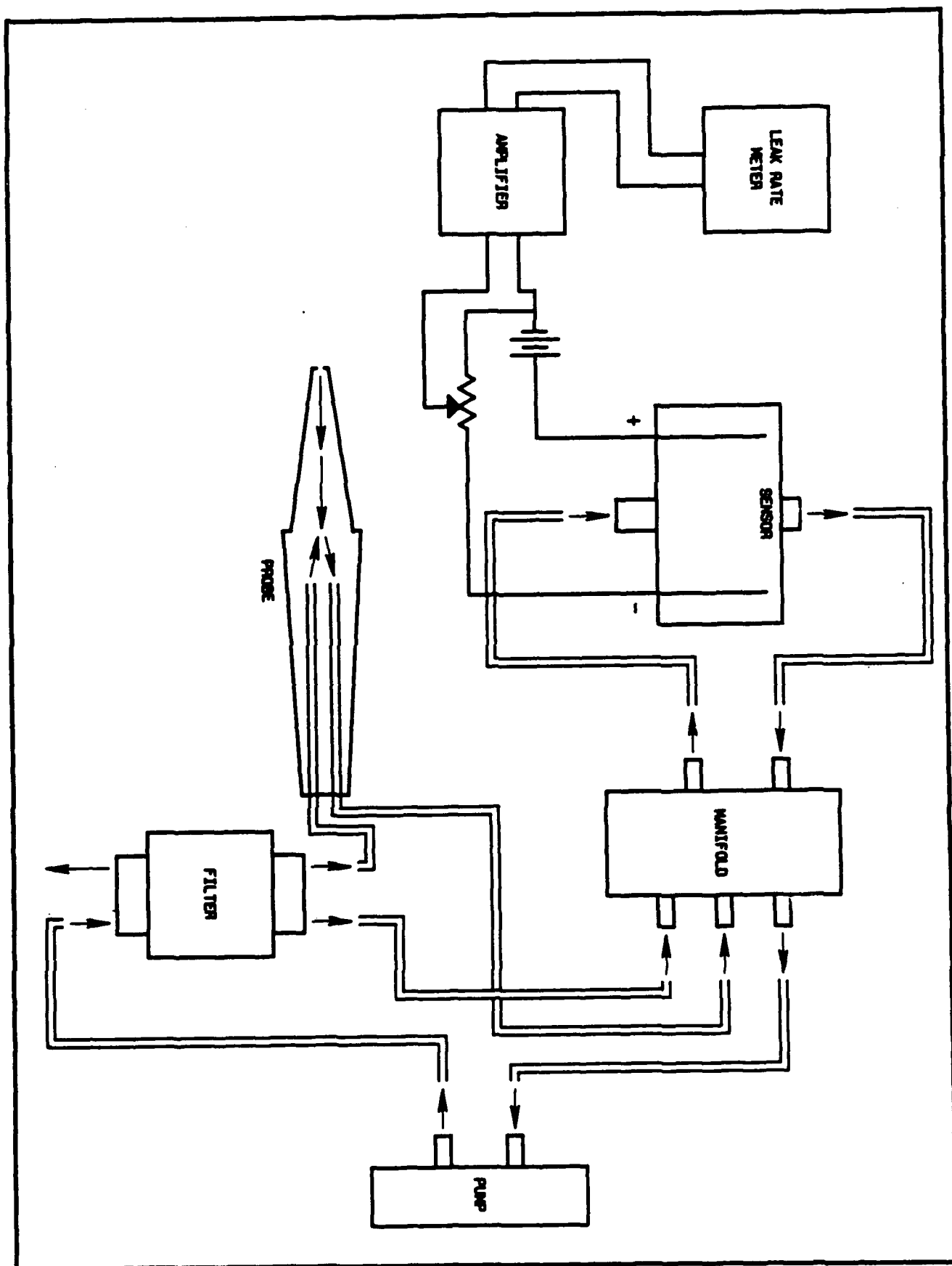
An established task of the Naval Medical Research Institute (NMRI) is reevaluation of the current Interim Air Purity Guidelines for submarine Dry Deck Shelter (DDS) Operations (1) with recommendation for revision as appropriate. At present, these guidelines incorporate three methods of gas analysis: 1) the Central Atmosphere Monitoring System-I (CAMS-I) that is installed on submarines, 2) the Portable Photoionization Detector (PID), which is normally carried on board, and 3) chemical detector tubes. One goal of this evaluation is to replace many of the detector tubes with alternative methods of chemical detection that are more reliable. This change would be particularly directed toward compounds that are not easily detected by the PID such as many halogenated compounds (e.g., numerous industrial cleaning solvents and Freons).

One instrument that has been proposed as suitable for measurement of halogenated hydrocarbon is the Ferret® halogen leak detector (2). This detector was originally designed and manufactured by General Electric, but is now made by the Yokogawa Corp. (Shendoah, CA). It is a portable unit with a hand-held probe designed for detecting leaks in industrial pressurized or vacuum systems where halogen gases are used. It is important to note that the Ferret® is marked as a sensitive leak detector and not as a high precision analytical instrument. Briefly, the detector operates via the production of an electrical current between a specially-treated ceramic emitter and a platinum collector in the presence of a halogen-bearing gas. The response is read off a 0 to 10 full-scale meter. A prior study (2) suggested that the Ferret® had adequate sensitivity (in the ppm range) for detecting hazardous levels of halogenated hydrocarbons in divers' breathing air. A recommended

procedure for doing this was presented. On this basis, it was thought possible that the Ferret® could be incorporated into the Air Purity Guidelines. However, on the negative side, the Ferret® employs a rather complex airflow system containing a probe for sampling, pump, tubing, charcoal filter, manifold, and sensor (see Fig. 1). This system produces two 1:10 dilutions in the sample gas as it flows from the sample site to the detector. Such a system with its many tubing connections appeared to have high potential for leaks and for instability due to changes in air flow.

The initial plan was to determine whether the Ferret® could be used for screening breathing air in a manner similar to that with the PID. The sensitivities for all detectable compounds specified in the Air Purity Guidelines (1) would be first established relative to some common, comparatively safe compound like a Freon. Then, based on this information and the DDS limits defined in the Guidelines, a given Ferret® reading (after calibration with the reference Freon) could be used to selectively rule out potential contaminants. Examination of the tables in the Air Purity Guidelines indicated approximately 10 halogenated compounds that are thought to be potential contaminants with DDS limits (values that cannot be exceeded if the gas is to be considered safe) ranging from 1 to 250 ppm. The usefulness of the Ferret® in this application would depend on the determination of relative sensitivity factors that are constant for each compound.

The testing described below in this report was meant to be a preliminary screening to determine whether the Ferret® might have adequate reliability and accuracy to be a useful device for incorporation into the Air Purity Guidelines. It was understood that additional testing would be necessary



before actual procedures could be developed for use of the Ferret® in the Fleet.

#### METHODS AND RESULTS

The instrument used in testing was the General Electric Ferret®, type H-25B, which had been purchased by NMRI several years earlier but had not been extensively used prior to this. Operating procedures were followed according to the instruction manual (3). Zeroing the instrument with a halogen-free gas, replication, and maximization of the meter response to increase the signal/noise ratio were some of the standard analytical techniques used during the test. The instrument response was adjusted both by a sensitivity switch ("gain") that amplifies the Ferret® output, and a potentiometer that adjusts the temperature of the sensor. According to the manual (3), the sensor response increases as the sensor temperature is increased, but the sensor life decreases. For our testing, the instrument was operated with both the sensitivity and temperature adjustments in mid-range as recommended in the manual. In addition, the automatic zeroing function of the Ferret® was turned off during tests by depressing a push-button switch that is mounted on the probe. This function would have interfered with low level halogen detection.

For convenience, 6 gas mixtures that were already in use in our laboratory were chosen for testing. The specific mixtures were Freon 11 (approximately 10 ppm), Freon 12 (10 ppm), Freon 113 (5, 20, and 100 ppm), and 1,1,1 Trichloroethane (10 ppm). All gravimetric standards were prepared in hydrocarbon-free air or He and certified to  $\pm 2\%$  relative of stated value (Scott Specialty Gases, Plumsteadville, PA). These concentrations were at the lower end of the range in DDS limits. Gas was delivered to the probe of the analyzer using a high-purity regulator (with stainless-steel diaphragm). A

brass luer adapter that had been screwed onto the outflow end of the regulator allowed a 5-ml plastic syringe barrel to be attached. The Ferret® probe could then be inserted into the gas flowing out of the syringe at 1 atmosphere pressure absolute. This gas was drawn into the probe by the suction action of the pump contained in the electronics unit.

Initial testing concentrated on measuring sensitivities of the three halogenated compounds relative to Freon 113 (using the 5 ppm Freon 113 as the reference mixture). Purer et al. (2) presented some data on the Ferret® response to increasing numbers of halogen atoms on a molecule (e.g., chlorines: methyl chlorine, methylene chloride, chloroform, carbon tetrachloride) based on gas standards for 17 halogenated hydrocarbons with concentrations ranging from 4-7 ppm in nitrogen. It had been concluded that the detector output increased with increasing chlorine, bromine or iodine atoms, and this increase was linear in most cases. For our purpose, the relative sensitivity of a given chemical species, "A", was calculated in relation to the reference gas in the following manner.

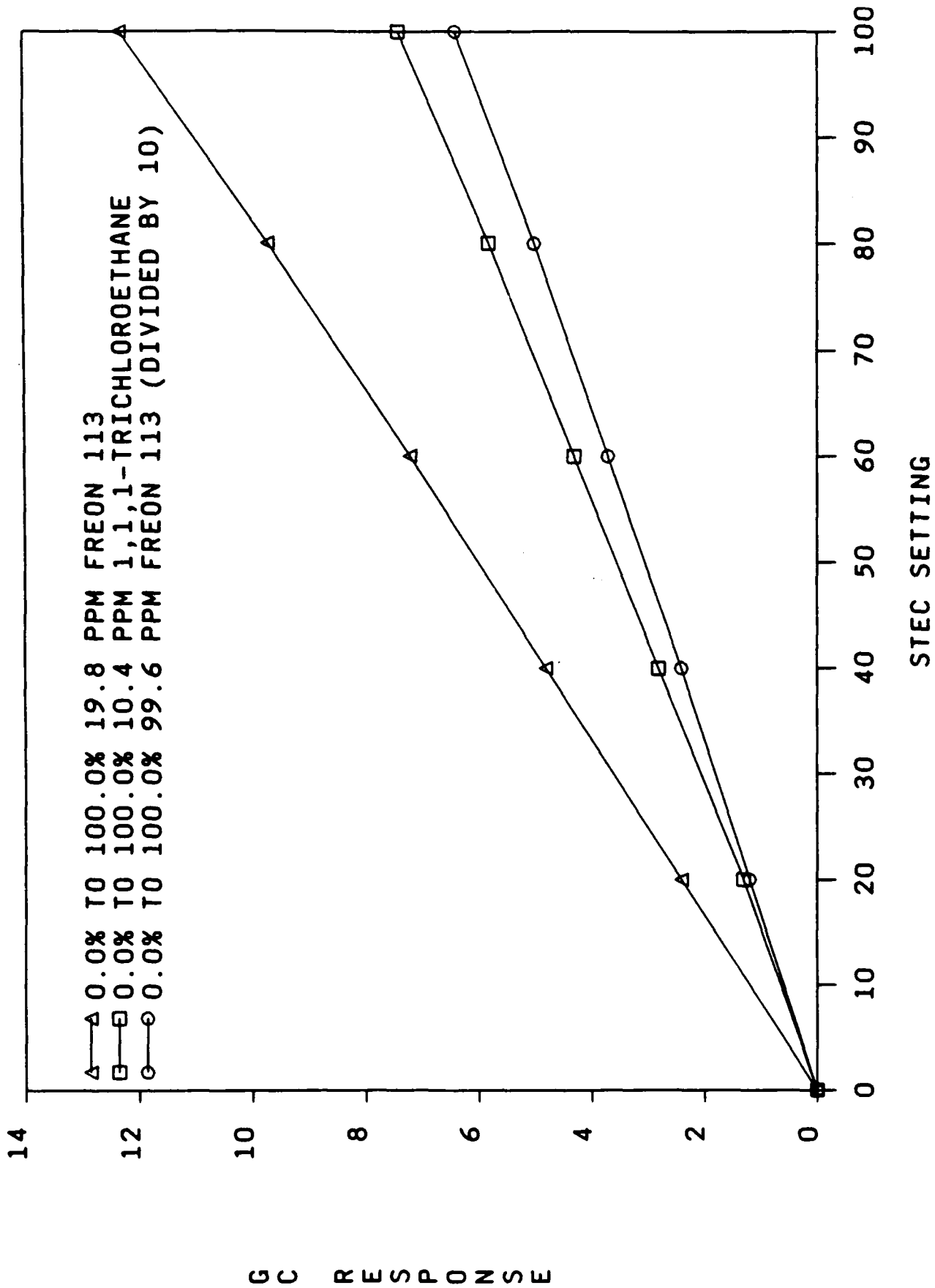
$$\text{Relative Sensitivity} = \frac{\text{Meter Response of "A"/Concentration of "A"}}{\text{Meter Response of Reference/Concentration of Reference}}$$

Replicated measurements were repeated on a number of days over a period of a month. Results indicated adequate although different sensitivity of the Ferret® for the four chemicals tested at concentrations of 5-10 ppm (Table 1). There was overall good intra-day precision with an observed range in readings of about 0.3-0.4 meter units when measurements with the same gas mixture were repeated over a period of a day without any adjustment in gain settings. This

precision was influenced by the inability to resolve needle deflection differences of less than 0.1 on the 0 to 10 units full-scale meter. However, these small precision errors could produce large relative variations in the computed relative sensitivity values, particularly with a fairly insensitive chemical such as Freon 12. For Freons 11 and 12, inter-day variation in sensitivity measurements appeared to be within daily precision limits of the instrument. The larger range in sensitivities for 1,1,1 Trichloroethane probably reflects the greater difficulty obtaining a stable reading with this chemical compared to the other three chemicals.

The next step in testing was to determine whether the response of the instrument was linear with changing concentration of a given chemical. Purer et al. (2) did not report any data on the Ferret® response as the concentration of a specific chemical increased. Although a Yokogawa representative did not have any information regarding linearity specifications for the Ferret®, the Ferret® manual (3) contained operating instructions that assumed linearity over a large range of leak rates.

Linearity tests were performed using a precision gas divider (STEC model SGD-710, Horiba Instruments Inc., Ann Harbor, MI). This device allowed the blending of a calibration gas of known concentration with a diluent gas in 10 equal steps from 0% to 100% of the original concentration. A number of tests were performed using the three mixtures: 10 ppm 1,1,1 Trichloroethane, and 20 ppm and 100 ppm Freon 113. Testing initially consisted of measuring the gas divider concentration simultaneously with the Ferret® and a gas chromatograph (GC) equipped with a flame ionization detector to certify the performance of the STEC. After the gas divider was found to be accurate (Fig. 2), GC analysis was not always performed concurrently with Ferret measurement. The

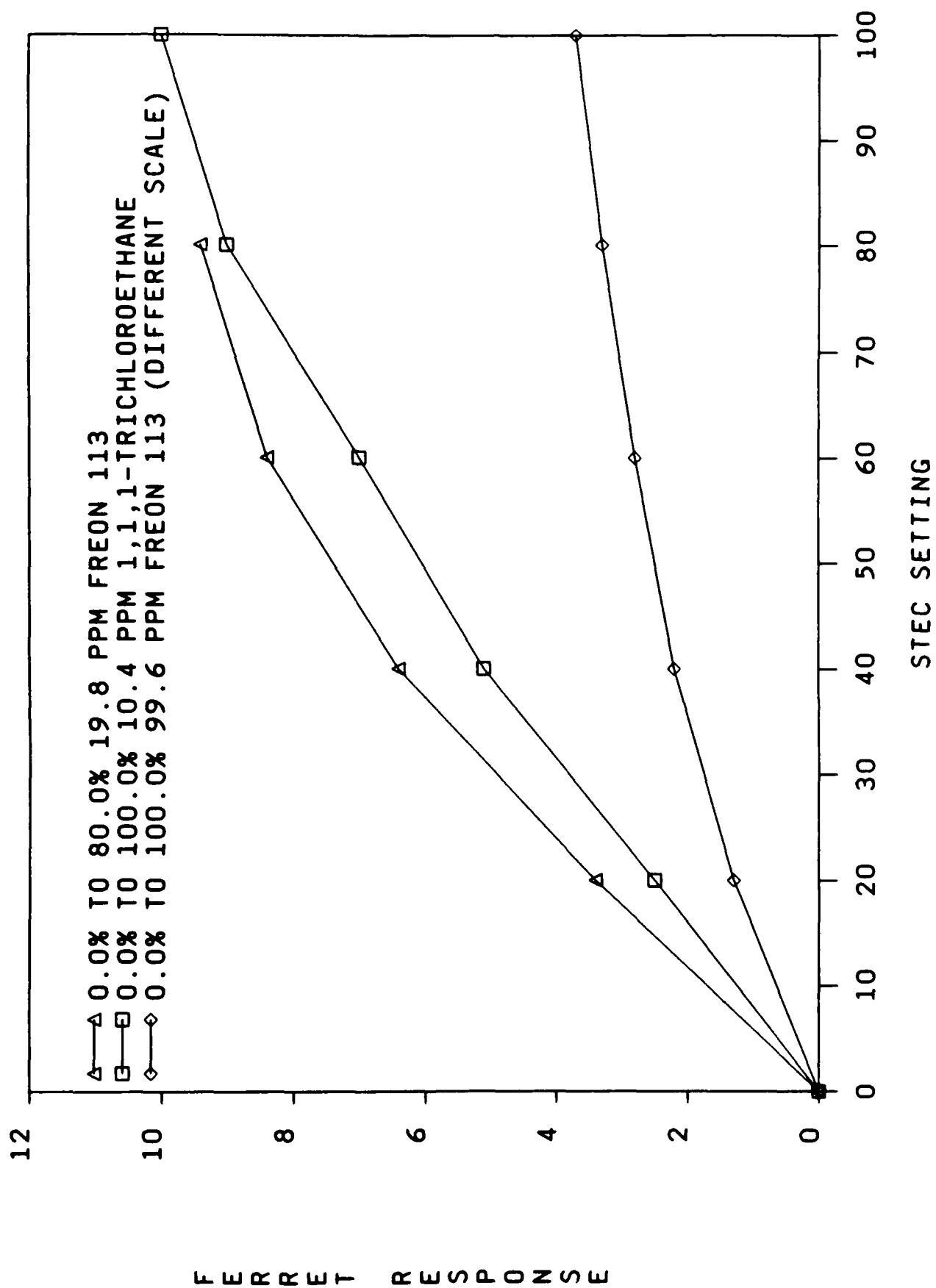


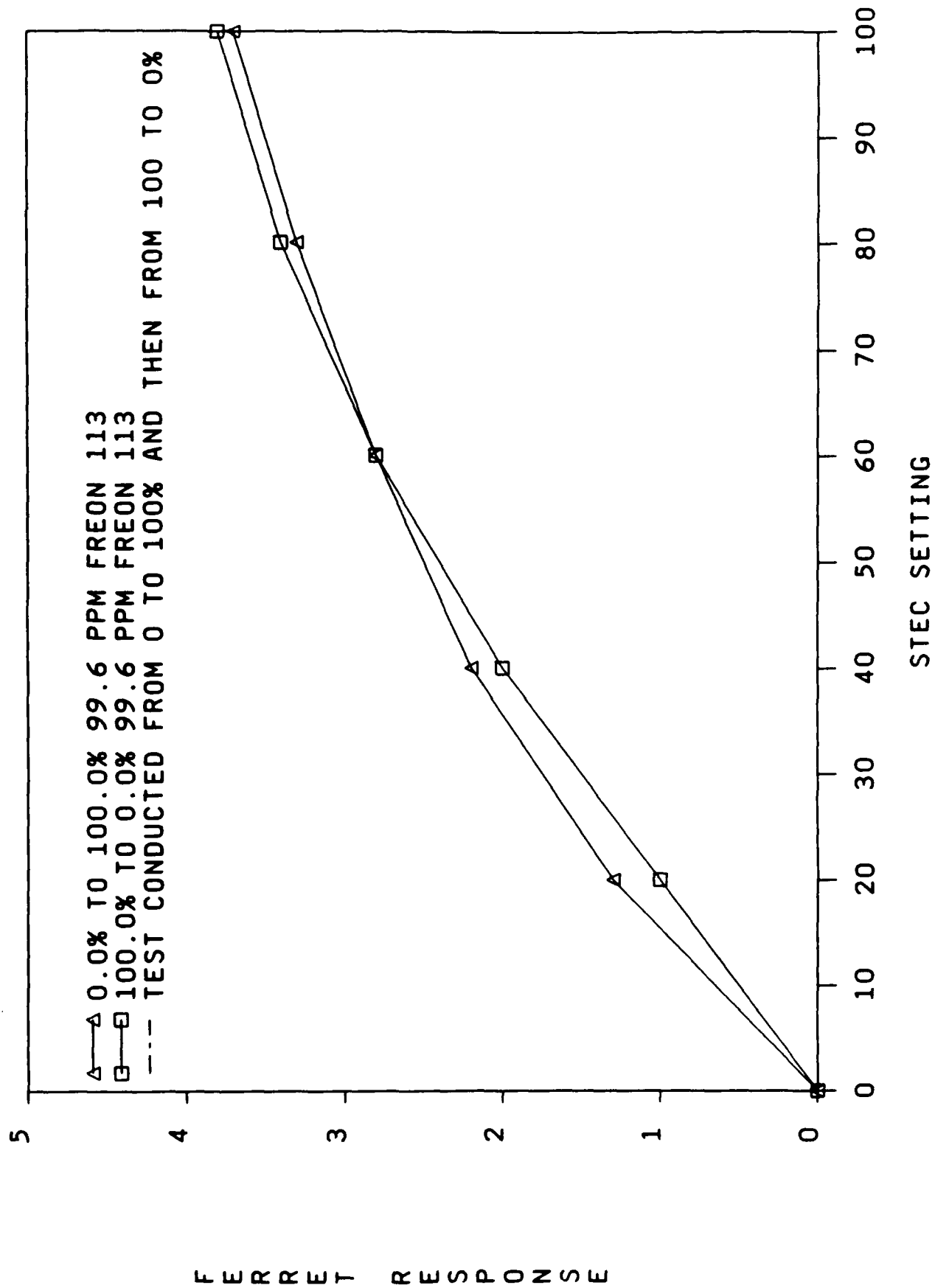
Ferret® response was found to be non-linear, with all three mixtures, with the observed response lower than expected at higher concentrations (Fig. 3). This was true with either increasing or decreasing concentrations (Fig. 4). The measurement error associated with assuming a linear response with changing concentration was substantial. For example, based on full-scale calibration with 100% of the original concentration, the measured concentrations of mid-range levels were 20-35% (relative) higher than actual values.

#### DISCUSSION AND CONCLUSIONS

The Ferret® is sold as a sensitive halogen leak detector and is not promoted as a high precision analytical instrument. The device appears to have adequate sensitivity for use in detection of halogenated hydrocarbons down to the ppm level. However, the Ferret® design with its complicated airflow system and gas dilutional process appears to have great potential for leaks and instability. Thus, the reliability of such a device operated in the field under less than optimal conditions would be questionable from merely a design standpoint.

The incorporation of the Ferret® into the current Interim Air Purity Guidelines for DDS operations is predicated on the determination of constant relative sensitivity values for each of the potential halogenated contaminants. However, our measured sensitivities not only seemed to vary somewhat from day-to-day but also disagree substantially with values reported by Purser et al. (2) as well as the manufacturer, Yokogawa Corp. (Table 2). In fact, the values from these two sources were also inconsistent with one another. The observed non-linear response of the Ferret® to increasing halocarbon concentration may explain much of this disagreement. Relative responses would be expected to vary with the concentrations of the test





mixtures precisely because of this non-linearity. This follows from the definition of relative sensitivity, which relates the response per unit concentration of one chemical to that of another chemical. Clearly, these relative values would change if sensitivities for individual species were not constant (i.e., non-linear). Unfortunately, the reason for this observed non-linearity is not known at this time.

Assuming the performance of the one Ferret® tested is representative of all such instruments, we do not recommend further testing of this device. Because of its non-linearity and resulting variation in relative sensitivities, simple use of the Ferret® to test for safety of gas during DDS operations will not be possible.

#### REFERENCES

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2. Purer, A., Deason, G.A., and Taylor, R.J., Total halogenated hydrocarbons in divers breathing air, NCSC TR383-83, Naval Coastal Systems Center, Panama City, FL, 1983.
3. The Ferret® Leak Detector, Operating Instructions. #4540K15-001 HM1. Yokogawa Corp. of America, Shendoah, GA, 1985.
4. Leak Detector Manual, #ID-4816D. General Electric, Lynn, MA, 1983.

Table 1. Relative sensitivities determined with the Ferret® and calculated using Freon 113 as the reference gas. Values are means (SD) of values determined over several hours on 4 different days over a period of 1 month. Data reflect day-to-day variability in measurements.

Test Day	n	1,1,1 Trichloroethane	Freon 11	Freon 12
1	6	1.0 (0.1)	1.2 (0.1)	0.6 (0.1)
2	4	0.9 (0.1)	1.0 (0.1)	0.4 (0.1)
3	4	1.6 (0.2)	1.1 (0.1)	0.3 (0.1)
4	5	2.3 (0.3)	1.4 (0.2)	0.4 (0.1)

$$\text{Relative Sensitivity of "A"} = \frac{\text{Meter Response of "A"/Concentration of "A"}}{\text{Meter Response of Reference/Concentration of Reference}}$$

Table 2. Comparison of Relative Sensitivities (using Freon 12 as the reference gas) measured by NMRI with those reported by Purer et al., 1983 and by Yokogawa Corp. NMRI values are taken from Table 1 but re-calculated relative to Freon 12.

Source	1,1,1 Trichloroethane	Freon 11
Purer	1.8	2.0
Yokogawa	3.0	3.4
NMRI - day 3	5.3	3.7
- day 4	5.8	3.5

Yokogawa values were obtained via telephone conversation with a company representative October 1988.

## FIGURE LEGENDS

- Figure 1. Schematic of air flow system of Ferret® (Adapted from Ref. (4)). Arrows indicate path of air flowing through Ferret .
- Figure 2. Linearity of the STEC gas divider as shown by GC response (peak area) vs. STEC setting. Calibration gas: 10.4 ppm, 1,1,1 Trichloroethane, 19.8 ppm Freon 113, 99.6 ppm Freon 113.
- Figure 3. Ferret® response vs. STEC gas divider setting. Calibration gases: 10.4 ppm 1,1,1 Trichloroethane, 19.8 ppm Freon 113, 99.6 ppm Freon 113.
- Figure 4. Ferret® response vs. STEC gas diver setting. Calibration gas: 99.6 ppm Freon 113. Experiment performed adjusting STEC divider from 0 to 100 and then from 100 to 0.